

Mesogen-jacketed liquid crystalline polymers substituted with oligo(oxyethylene) as peripheral chain

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ABSTRACT

Mesogen-jacketed liquid crystalline polymer (MJLCP) is a typical rod-shaped macromolecule. Its unique molecular architecture allows one to tune the geometric parameters of the macromolecular rod. Moreover, the rod surface chemistry can be controlled by designing the peripheral groups of the lateral mesogens. In previous work in this system, short alkyl chains have been used and the resultant macromolecular rods therefore have a hydrophobic surface. In this paper, we report using oligo(oxyethylene) groups as the peripheral groups of the lateral mesogens. Poly[[2,5-bis[4-methoxyoligo(oxyethylene)phenyl]oxycarbonyl]styrene] (PnEOPCS) with different oligo(oxyethylene) chain length has been synthesized. These oligo(oxyethylene) groups led to macromolecular rods with hydrophilic surface. Differential scanning calorimetry, polarized light microscopy, and one-/two-dimensional wide-angle X-ray diffraction experiments were carried out to study the phase structures and phase behaviors of this series of polymer. The existence of flexible polar groups lowered the glass transition temperatures of PnEOPCS. All polymers studied showed supramolecular columnar nematic or hexatic columnar nematic phase, which arose from the parallel alignment of the polymer supramolecular rods. The diameter of the cylindrical building block increased with increasing the length of the oligo(oxyethylene) groups. The macromolecular rod surface can be further tuned by complexation the oligo(oxyethylene) with lithium salts. Detailed study showed that this complexation also tremendously affected the liquid crystalline phase of the polymer.

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1. Introduction

Soft matter self-assembly is an essential part of nanotechnology and it offers one of the few practical strategies for making nano-scale ensembles [1–5]. By tuning the shape and chemical nature of soft matter, complex structures can be achieved. A large number of exotic molecular assembly systems, including mushrooms and amphiphilic discs, have been designed. Shape and chemistry tunability is crucial to designing molecular building blocks for targeted soft matter. For example, for an ideal rod-forming system, shape parameters, such as length, diameter, and rigidity of the rods, chemistry of the core as well as the shell, can be easily tuned by judicious selection of the chemical synthesis strategy and proper molecular design; hence the self-assembly behavior of rods can be

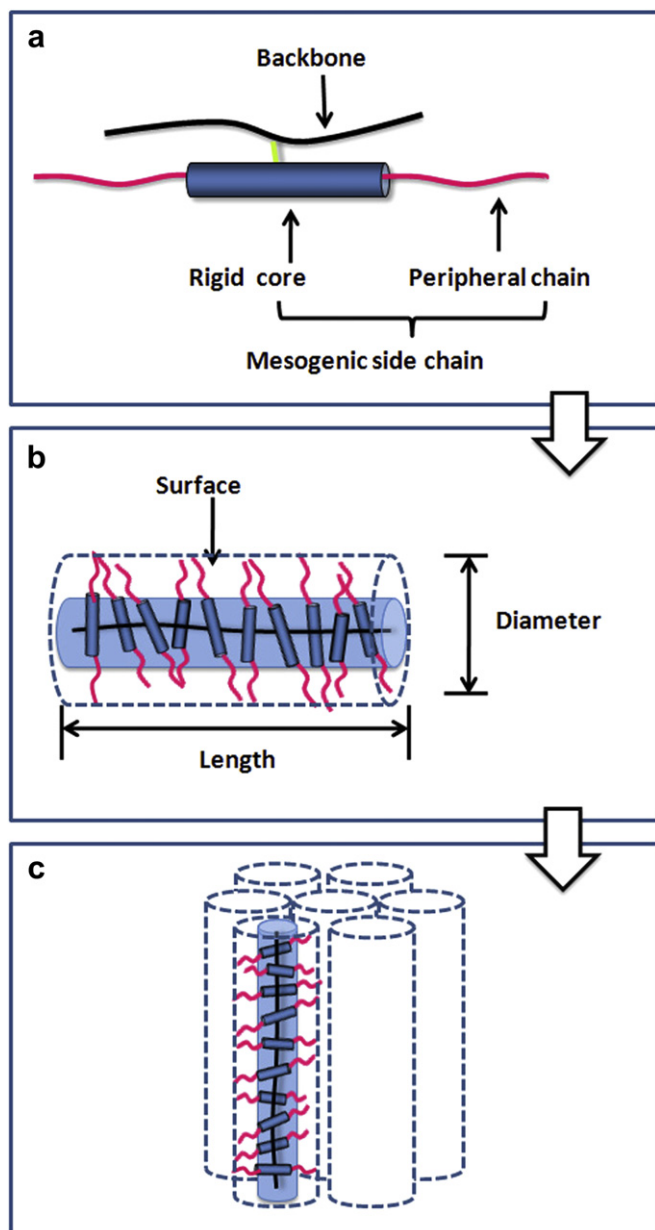
thoroughly investigated. Of interest is that many of these designing strategies are biomimetic because synthetic molecular rods share many similarities with their natural counterparts [6–10].

From a synthetic standpoint, it is challenging to design and synthesize an ideal “rod” mentioned above. Some rod parameters, such as rod length, can be readily controlled by tuning the polymer molecular weight (MW). Others, such as rod diameter and surface chemistry, cannot be easily controlled in many rod-forming systems. As a model rod-shaped polymer, mesogen-jacketed liquid crystalline polymer (MJLCP) offers a good opportunity to tune all the aforementioned structural parameters (Scheme 1) [11–13]. Based on previously reported work, in an MJLCP, the laterally attached mesogens are nearly perpendicular to the rod axes [14,15]. Because the spacer is short, the rigid mesogens intimately wraps the backbone, hence the whole polymer chain exhibits a semirigid rod feature [16,17]. From Scheme 1, it is evident that the rod length can be controlled by the MW of the MJLCPs [6]. Moreover, the diameter and surface chemistry of the rod can be tuned by altering the structure of laterally attached mesogens. For instance, when the

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Scheme 1. Schematic illustration of Mesogen-jacketed Liquid Crystalline Polymers (MJLCPs): (a) The general molecular structure of MJLCP containing polymer backbone and laterally attached mesogenic side-chains, which composed of with the rigid-core and flexible peripheral chains; (b) The jacketing effect renders the polymer chain a semirigid rod feature. The shape parameters of the rod, including diameter, length, and surface chemistry, are related to the laterally attached mesogenic chain; (c) Supramolecular columnar phase structure is frequently observed in MJLCP system, due to parallel alignment of these semirigid polymer chains.

side attached mesogen contains three phenyl rings, the rod diameter is around 2 nm. When the side attached mesogen contains five phenyl rings, the rod diameter reaches $\sim 3\text{--}4$ nm [18].

Surface chemistry of the rod could be controlled by the substituted peripheral groups. In the previously reported MJLCP systems, the flexible terminal groups connecting to the mesogens are nonpolar alkyl chains. Oligo(oxyethylene)s, exhibiting not only polarity, but also flexibility, hydrophilicity, and the ability to form complexation with Li^+ , have been used in molecular engineering of rigid rod-like conjugated polymer systems, in order to improve solubility in hydrophilic solvents [19], or to obtain “hairy rod” polymers for polymer electrolyte applications [20,21]. However,

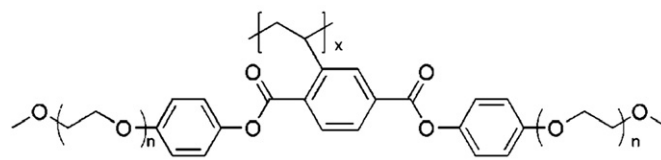
they have not been used as peripheral groups in MJLCP systems. As shown in Scheme 2, employing oligo(oxyethylene) in MJLCPs can directly lead to core-shell macromolecular rods with hydrophilic shells; these rods are significantly different from all the previously reported MJLCPs. Moreover, oligo(oxyethylene) could affect the overall phase behavior of the LCP in two ways. First, The *gauche* conformation oligo(oxyethylene) makes its cross-sectional area [22] larger than that of a normal calamitic mesogen ($0.21\text{--}0.22$ nm²). This cross section mismatch could destabilize mesogen close packing in calamitic LCs [23]. However, in MJLCP systems, since the mesophase is formed because of supramolecular self-assembly of the entire polymer chains, replacement of alkyl groups by oligo(oxyethylene) might not affect the mesophase formation as significantly. Secondly, complexation of oligo(oxyethylene) with lithium salts could offer us more opportunities to tune the mesophase structure and to build up multi-functional systems based on MJLCPs. It should be noted that if fluorocarbonyl groups or oligosiloxane chains partially substitutes aliphatic chains in side-on side chain liquid crystalline polymer (SCLCP) systems [24–28], the incompatibility of fluorocarbonyl group or oligosiloxane chain with central aromatic core would finally induce the mesophase transformation from nematic phase, a predominant mesophase structure existed in side-on SCLCP, to smectic phase, indicating the chemical structure of flexible peripheral chain is important to the mesophase formation. So the question is how oligo(oxyethylene) groups influence the phase behavior of an MJLCP shown in Scheme 2.

It is the goal of this paper to investigate LC phase behaviors of a series of MJLCPs with oligo(oxyethylene) chain as flexible tails of the jacketed mesogens. In order to compare with reported MJLCP systems having alkyl chain as the mesogen tails, we used the same polyethylene backbone in our new series and kept the mesogenic core structure identical to that of the reported systems. The repeating unit number of oxyethylene group was varied from 1 to 4. The target polymer structure was listed in Scheme 2.

2. Experimental section

2.1. Materials

The compound of vinylterephthalic acid was synthesized using the method previously reported [29,30]. Chlorobenzene was purified by washing with concentrated sulfuric acid to remove thiophene, followed by washing with water, and then dried and distilled. Cuprous bromide (CuBr) was purified by stirring in glacial acetic acid, filtering, and washing with ethanol and was then dried under vacuum. 4-(Dimethylamino)pyridine (DMAP) (99%, Acros) 1-bromoethylbenzene (BEB) (97%, Acros), *N,N,N',N''*-pentamethyldiethylenetriamine (PMDETA) (>98%, TCI), 1-bromooctane (99%, J&KCHEMICA), tri(ethylene glycol) monomethyl ether (97%, Acros), tetra(ethylene glycol) monomethyl ether (99%, Aldrich), and other reagents (Beijing Chemical Works) were used as received without further purification.



PnEOPCS, n=1-4

Scheme 2. Chemical structure of PnEOPCS ($n = 1\text{--}4$).

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